



FTIR spectroscopy study of the reduction of carbon dioxide on lead electrode in aqueous medium

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ABSTRACT

The electrochemical reduction of carbon dioxide at a lead electrode was studied in alkaline aqueous medium. Chronoamperometry experiments combined with *in situ* reflectance spectroscopic measurements were performed after bubbling CO₂ in an alkaline solution up to a pH value of 8.6. Combining information from *E*–pH diagram which provided the predominant species in the bulk solution and the adsorbed species determined spectroscopically, the results showed the only synthesis of formate from the electroreduction of hydrogenocarbonate. The identification of the different electroactive species allowed a reaction mechanism to be proposed for the transformation of hydrogenocarbonate into formate on the lead cathode.

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1. Introduction

Carbon dioxide is now known to be a major cause of global warming. Although the technology used for its capture and storage is of a great interest, it can be considered that its widespread availability makes it as a valuable reactant for the synthesis of chemical products [1–9]. Metal electrodes such as Cu, Pb and Zn have been extensively employed in the electrochemical reduction of CO₂. Depending on the metal used as cathode the final reaction products can vary considerably. This wide range of end products extends from hydrocarbons (methane, propane, ethylene, etc.) to oxygenated molecules, the most important of which are methanol, ethanol, and formic and oxalic acids. The reaction product distribution is very sensitive to various parameters such as applied potential, buffer strength and local pH, local CO₂ concentration, CO₂ pressure and the surface crystal structure of the electrode [5,8,10–20]. In other studies, on several transition metal electrodes (Ni, Pd, Pt, etc.) carbon monoxide was mainly formed [21–27]. Rodes et al. carried out a series of FTIR studies of CO₂ reduction on Pt single crystals and CO is the main reaction product observed [28–30]. Recently, there have been many extensive studies on the electroreduction of CO₂ in different (protic or aprotic) solvents in which the solubility of the reactant varied. For instance methanol

was found to be a better solvent of CO₂ than water, particularly at low temperatures (CO₂ is 8–15 times more soluble at 20 °C) [20–25]. However, the conversion of CO₂ on Pb or Cu electrodes, although leading to the formation of formic acid, also produces other organic molecules, decreasing the selectivity and complicating the separation of the end products [9,13,31–36].

Among high hydrogen overvoltage electrodes with negligible CO adsorption (Hg, Cd, Pb, In and Sn) that could reduce selectively CO₂ to formate in aqueous medium, lead appears to be the most suitable cathode material for an industrial application [7,33]. There is some controversy in the reduction mechanism concerning the nature of the reacting species. Numerous reports in the literature have established that only dissolved CO₂ takes part in the reduction, and not HCO₃[–] and CO₃^{2–} ions from the solution [32,37–43]. Osetrova et al. [44] studied the electroreduction of carbonate solutions at different cathodes such as copper and platinum. Methane, ethylene, formaldehyde, methanol and other organic reaction products were determined by chromatography. They assumed that carbonate reduction occurred through the intermediate formation at the anode of percarbonate ions when the process was achieved at low temperatures in a cell without a diaphragm. Moreover, other studies have investigated this reaction in different solutions and found that the reduction was influenced by the presence of HCO₃[–] [45]. To investigate this reaction, the present work is mainly focused on an *in situ* FTIR spectroscopy study of the electrochemical reduction of CO₂ in aqueous medium on a lead electrode. Different *in situ* IR reflectance spectroscopy

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techniques were used to identify the electroreductive species and provide evidence of formate as the sole organic reaction product.

2. Experimental

2.1. Three electrode conventional cell

In order to characterize the electrochemical behavior of the reactant, voltammetric experiments were carried out in an one-compartment conventional three electrode Pyrex cell ($V = 15 \text{ cm}^3$) at $21 \pm 1^\circ \text{C}$. The working electrode consisted of a lead wire. The current densities were normalized to the geometric surface area of 0.42 cm^2 . A vitreous carbon plate and $\text{Hg}/\text{Hg}_2\text{Cl}_2/\text{KCl sat.}$ (SCE) served as counter and reference electrodes, respectively. SCE was separated from the solution by a Luggin–Haber capillary tip. Electrochemical measurements were performed with a PC controlled AutoLab PGSTAT 302 Electrochemical Interface.

2.2. Three electrode spectroelectrochemical cell

A special three electrode spectroelectrochemical cell was designed with a CaF_2 IR transparent window allowing the beam to pass through a thin electrolyte layer and to be reflected with an incidence angle of 65° . The working electrode was a Pb disc of 8 mm diameter. This electrode was mechanically polished to a mirror-finish with alumina (up to $0.3 \mu\text{m}$). The counter electrode was a vitreous carbon plate and the reference electrode was $\text{Hg}/\text{Hg}_2\text{Cl}_2/\text{KCl sat.}$ (SCE), separated from the solution, as described above. IR reflectance spectra in the wave number region $1000\text{--}3000 \text{ cm}^{-1}$ were collected by a Fourier transform infrared spectrometer Bruker IFS 66v/S. This apparatus was equipped with a helical global light source and a liquid N_2 -cooled mercury–cadmium–telluride (MCT) narrow-band detector (Infrared Associates). Data acquisition and processing were performed using a computer with OPUS 5.5 software.

Two different methods were used to obtain FTIR spectra: Single Potential Alteration Infrared Reflectance Spectroscopy (SPAIRS) and chronoamperometry measurements. This technique [46–48] which is suitable for detecting intermediates and reaction products consists in recording the reflectivities R_t at 50 mV intervals each during the first voltammetric scan at a sweep rate of 1 mV s^{-1} . Each IR spectrum is the Fourier transform of the average of 128 co-added interferograms. Spectra were calculated as the variation of absorbance due to the presence of a new product or the disappearance of a reactant at the electrode surface: $-\Delta A = \Delta R/R_0 = (R_{E2} - R_{E1})/R_{E1}$, where the “reference” spectrum, R_{E1} , was that recorded at a given potential, chosen in a domain where no reduction of electroreductive species was observed during the voltammetry measurement. In each case the reference spectrum was clearly noted for clarifying the calculation as described elsewhere [49]. As the potential was scanned from -1.0 to -1.8 V vs. SCE , with a sweep rate of 1 mV s^{-1} the reference spectrum was taken either at the initial potential limit (-1.0 V) or at the final potential limit (-1.8 V). When the reference spectrum was fixed at -1.0 V , positive and negative bands represent the production and consumption of species at the sample potential, respectively. Conversely, a reference spectrum chosen at the final potential limit (-1.8 V) involves positive and negative bands for the consumption and the formation of species at the sample potential, respectively.

With the second technique, spectra were recorded at different times ($t = 2, 5$ and 10 min) when the cathodic potential was set at a given value. For this technique, spectra were calculated as $-\Delta A = \Delta R/R = (R_t - R_{t=0})/R_{t=0}$, where the “reference” spectrum, $R_{t=0}$, was that recorded at $t = 0$. Both techniques allowed the detection of adsorbed species, intermediates and reaction products at the vicinity of the electrode surface and at the surface.

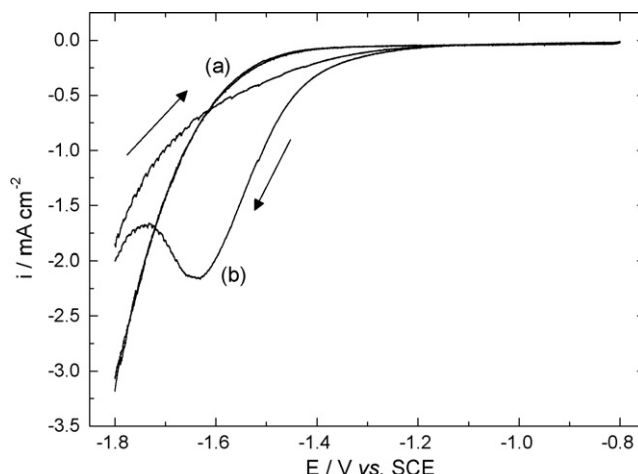


Fig. 1. Voltammograms of a Pb electrode in 0.1 M NaOH recorded at 1 mV s^{-1} . (a) In supporting electrolyte. (b) After bubbling CO_2 until $\text{pH} = 8.6$.

Supporting electrolytes were prepared with ultra pure water ($18.2 \text{ M}\Omega \text{ cm}$ at 20°C , MilliQ Millipore system). Suprapur NaOH , KHCO_3 and anhydrous K_2CO_3 were purchased from Merck and used as received. Carbon dioxide gas (99.5%) was purchased from L'Air Liquide.

3. Results and discussion

3.1. Voltammetry study

Cyclic voltammograms (CV) on the lead electrode in 0.5 M NaOH solution were recorded at a potential sweep rate of 1 mV s^{-1} and at 20°C in the absence (Fig. 1a) and the presence (Fig. 1b) of CO_2 . The bubbling of CO_2 was stopped at $\text{pH} = 8.6$ and the second voltammogram of Pb in Fig. 1b was recorded. The cathodic current starts increasing at -1.2 V vs. SCE . The maximum cathodic current (-2.2 mA cm^{-2}) was obtained at -1.6 V vs. SCE .

According to the $E\text{--pH}$ diagram reported by Hori and Suzuki [50], the predominant species at this pH are the hydrogenocarbonate ions, which means that this compound is reactive at the electrode surface. The increase in the current densities in Fig. 1b confirms the results in the literature that the reduction of CO_2 would effectively proceeds between a pH of 7 and 9, i.e. the domain of pH where HCO_3^- is the predominant species [50–52]. At $\text{pH} = 8.5$ the bubbling of CO_2 in the cell is stopped and the equilibrium states between $\text{CO}_{2\text{aq}}$, HCO_3^- and CO_3^{2-} can be described, as follows:

On the dissolution of gaseous carbon dioxide in water, a rapid equilibrium occurs:

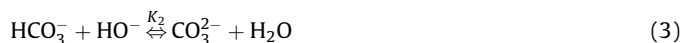


in alkaline solutions, the formation of carbonates is written as



$$K_1 = \frac{(\text{HCO}_3^-)}{(\text{CO}_{2(\text{aq})})(\text{HO}^-)} = 2.57 \times 10^{11}$$

then



$$K_2 = \frac{(\text{CO}_3^{2-})}{(\text{HCO}_3^-)(\text{HO}^-)} = 8.13 \times 10^3$$

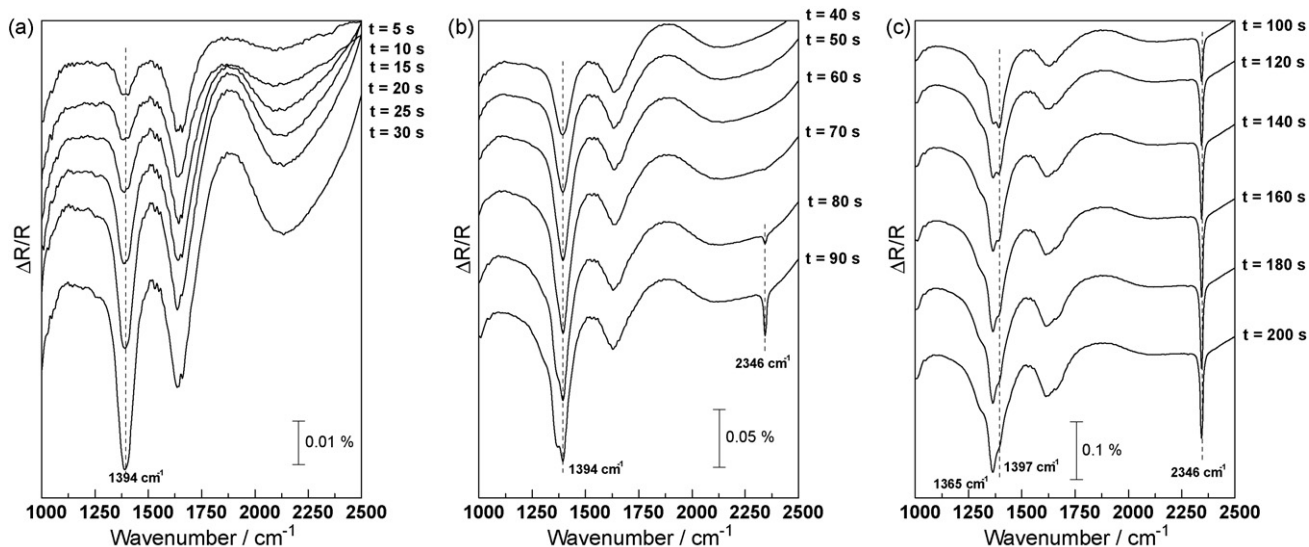


Fig. 2. FTIR spectra recorded in spectroelectrochemical cell without applied potential to a Pb electrode during CO₂ bubbling in 0.5 M NaOH; $\Delta R/R = (R_t - R_{t=0})/R_{t=0}$, the "reference" spectrum, $R_{t=0}$, was recorded at $t = 0$. (a) CO₂ bubbling between 5 and 30 s. (b) CO₂ bubbling between 40 and 90 s. (c) CO₂ bubbling between 100 and 200 s.

3.2. Spectroscopic study

Reference at open circuit: in order to determine the electro-reducible species in solution, *in situ* FTIR spectroscopy was used to follow the change in the nature of the species on the surface when bubbling CO₂ through an alkaline solution (0.5 M NaOH). As shown in Fig. 2, the spectra were recorded as a function of time at 5 s intervals each and without applied potential during a continuous bubbling of CO₂. These spectra are used as reference spectra for the following study using FTIR spectroscopy under potential.

Between 5 and 30 s (Fig. 2a), a negative band centered at 1394 cm⁻¹ can be observed and its intensity increases with time. These spectra can be compared to those depicted in Fig. 3 showing reference spectra of HCO₃⁻ (Fig. 3a) and CO₃²⁻ (Fig. 3b) diluted in KBr pellets. It is worth mentioning that KHCO₃ and anhydrous K₂CO₃ were used as received. As can be noticed in Figs. 2 and 3a,

there is another band centred at 1648 cm⁻¹ which can be ascribed to the H₂O molecules contained in the compound. The band at 1394 cm⁻¹ in Fig. 2a can be easily attributed to the formation of hydrogenocarbonate ions (Eq. (2)). With longer bubbling time (Fig. 2b and c), the appearance of a band due to CO₂ at 2346 cm⁻¹ can be noticed. A shoulder can be observed at 1365 cm⁻¹ but far from our present knowledge, it is not yet assigned.

Spectroscopy during voltammetry measurements: to determine whether species other than CO₂ undergo electroreduction at the Pb cathode in aqueous solution, the CO₂ bubbling was stopped before the appearance of its band centered at 2342 cm⁻¹, as shown in Fig. 2b. SPAIR spectra were calculated with the "reference" spectrum, R_{E1} recorded at -1.8 V vs. SCE. At this potential, although the voltammogram in Fig. 1 shows a reduction of hydrogenocarbonate ions superimposed to the H₂ evolution reaction, the SPAIR spectrum disappears since the reflectance at

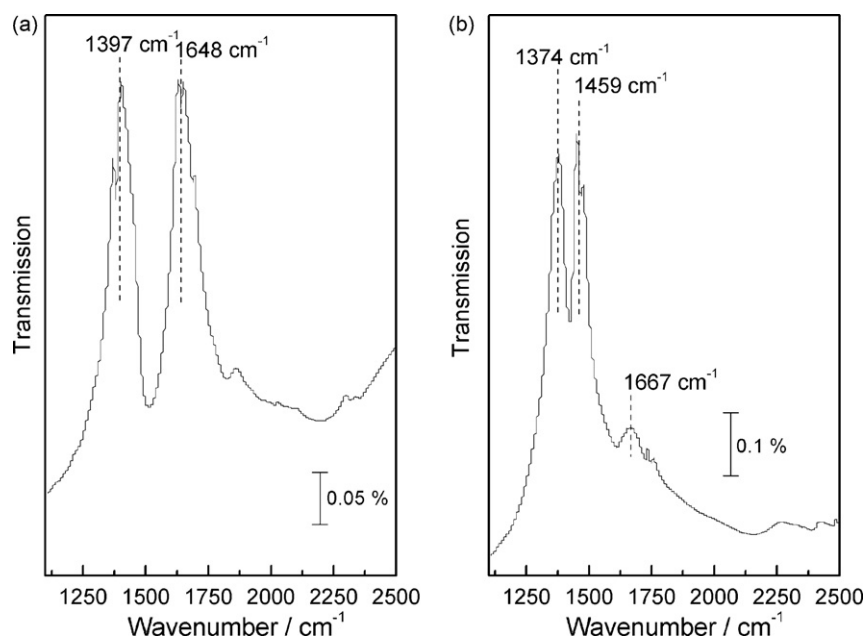


Fig. 3. Transmission spectra of KHCO₃ (a) and K₂CO₃ (b) diluted in KBr pellets.

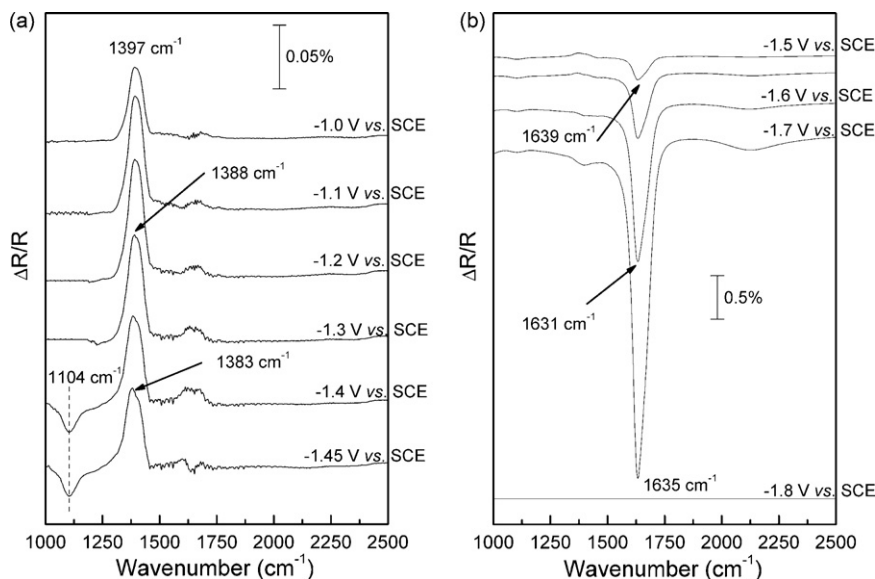


Fig. 4. SPAIR spectra on a Pb electrode after bubbling CO_2 in 0.1 M NaOH until pH = 8.6; $\Delta R/R = (R_{E2} - R_{E1})/R_{E1}$, where the “reference” spectrum, R_{E1} , was taken at $E = -1.8$ V vs. SCE. (a) Electrode potential from -1.0 V to -1.45 V vs. SCE. (b) Electrode potential from -1.5 V to -1.8 V vs. SCE.

-1.8 V vs. SCE, R_{E2} , is equal to that of the reference spectrum, R_{E1} , taken at this potential. Accordingly, a positive absorption band indicates the consumption of species and a negative absorption band means the production of species. For the sake of clarity SPAIR spectra are depicted in two parts (see Fig. 4a and b) with respect to the amplitude. In Fig. 4a, a band centered at 1397 cm^{-1} is ascribed to hydrogenocarbonate ions, which disappear more and more by reduction. A band centered at 1104 cm^{-1} which is present at -1.4 V vs. SCE is attributable to the ν_{CH} bending vibration of HCOO^- [53]. From -1.5 V vs. SCE the main band which can be observed at 1633 cm^{-1} (Fig. 4b), is attributed to the symmetric stretching mode $\nu_{\text{s}}(\text{OCO})$ from formate (HCOO^-). The band intensity due to the formate increases with increasing the potential up to -1.7 V vs. SCE confirming the production of formate ions and the low intensity of the band of hydrogenocarbonate ions which disappears by reduction.

The same spectra were calculated with a new reference spectrum taken at -1.0 V vs. SCE in order to follow the evolution of the absorption band centred at 1634 cm^{-1} . As can be observed in Fig. 5, the sign of this band ascribed to HCOO^- becomes positive. As evidenced, the reflectivity at -1.0 V well shows that no formate is produced at this potential, as shown in Fig. 1. The production rate of formate increases when the potential is going more cathodically; its band becomes higher than that obtained in Fig. 4b, but its sign is the opposite.

Moreover, Fig. 6 represents qualitatively as a function of potential the profile of the variation of band intensities attributed to hydrogenocarbonate and formate, respectively, issued from Figs. 4 and 5. Without taking into account the absorption coefficients of these species it can be well noticed that the production of formate correlated to the consumption of HCO_3^- . The consumption of HCO_3^- is complete at -1.6 V vs. SCE, which is consistent with the voltammetry results as the peak of reduction is observed at the same potential.

Further chronoamperometry/FTIRS measurements performed at -1.6 V vs. SCE allowed the band at 1634 cm^{-1} to be ascribed to HCOO^- . The reference spectrum is taken at $t = 0$, which means that the negative absorption bands correspond to the consumption of species, while the positive absorption bands can be ascribed to the production of species. The subtractively normalized IR spectra presented in Fig. 7 show that the electroreducible species of

dissolved CO_2 (herein HCO_3^-) are consumed in the diffusion layer of the solution to form formate ions. The intensity of the $\text{C}=\text{O}$ stretching band is however very high and, so that a contribution from the HOH deformation of interfacial water ($\sim 1600\text{ cm}^{-1}$) may be suspected.

Two characteristic bands can be observed, the first due to hydrogenocarbonate ions at 1393 cm^{-1} decreases with time, while the band intensity ascribed to formate at 1634 cm^{-1} increases with increasing formate concentration. As stated above, this latter band could comprise the contribution of the deformation of interfacial water ($\nu_{\text{H-OH}}$) located in the spectral range $1590\text{--}1800\text{ cm}^{-1}$ [53,54]. These values are in broad agreement with those obtained above, indicating a progressive disappearance with time of hydrogenocarbonate ions which produce exclusively formate ions.

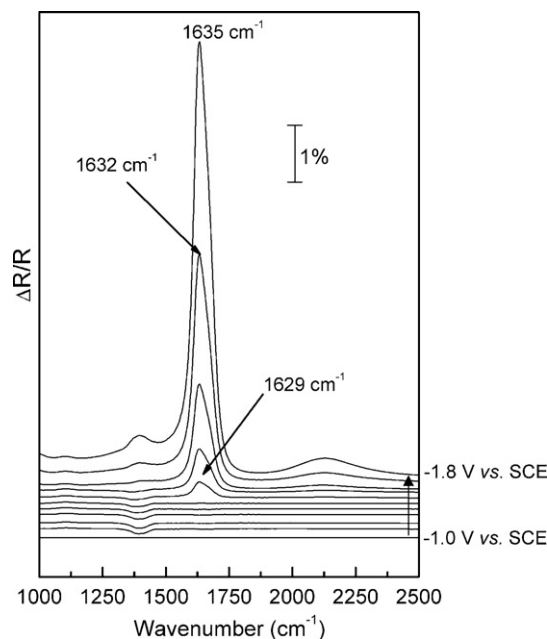


Fig. 5. SPAIR spectra on a Pb electrode after bubbling CO_2 in 0.1 M NaOH until pH = 8.6; $\Delta R/R = (R_{E2} - R_{E1})/R_{E1}$, where the “reference” spectrum, R_{E1} , was taken at $E = -1.0$ V vs. SCE.

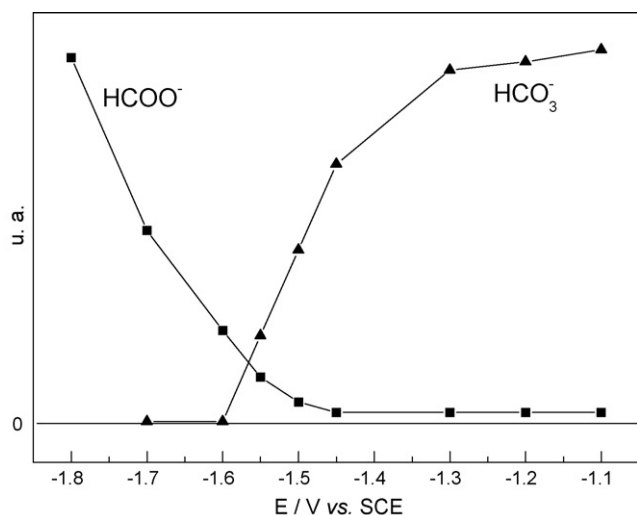


Fig. 6. Evolution of band intensities of HCO_3^- (▲) and HCOO^- (■) during a negative going scan of reduction on a Pb electrode. IR band intensities obtained from SPAIR spectra of Figs. 4 and 5.

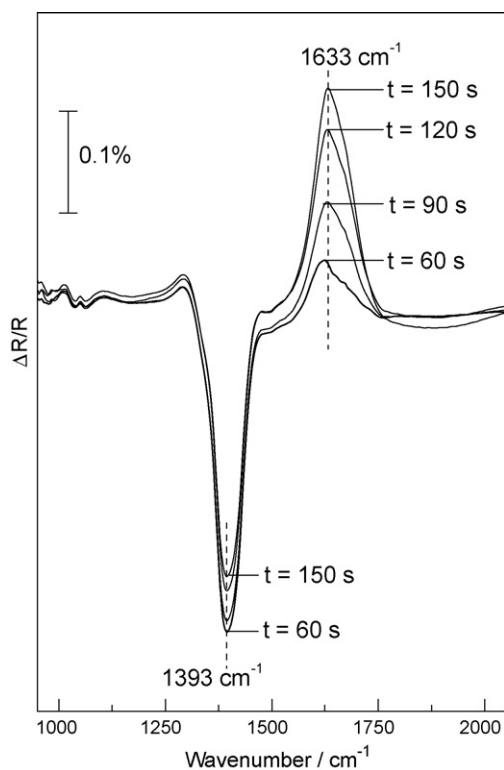


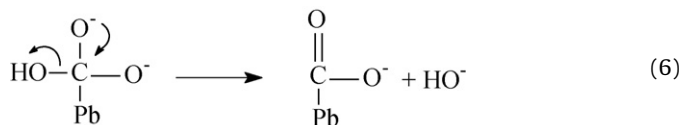
Fig. 7. Spectra in a 0.1 M NaOH solution after bubbling CO_2 until $\text{pH} = 8.6$, recorded during chronoamperometry measurements at -1.6 V vs. SCE on a Pb electrode; $\Delta R/R = (R_{ti} - R_{t=0})/R_{t=0}$, the “reference” spectrum, $R_{t=0}$, was taken at $t = 0$.

From the different spectroscopic results, it is possible to infer a reduction mechanism of the synthesis of formate from hydrogenocarbonate on lead electrode in alkaline solution. Taking into account the bands observed in spectra the various analyses focused on a selectivity of the reaction towards formate. From our results, it can be assumed that hydrogenocarbonate is reduced as follows:

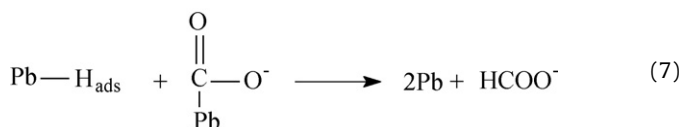
The first step is the reduction of the solvent, as shown by Chaplin and Wragg [6]:



Then the adsorption of hydrogenocarbonate at the lead sites could be written:



Hydrogenation then occurs by the interaction between two adsorbed species:



This assumed mechanism is almost analogous to that reported by Jitaru et al. [55] for the “sp” group metal cathodes. Additional evidences were provided herein, with the adsorbed species obtained by *in situ* FTIR spectroscopy. Actually, potential-dependent shifts of $\text{HCO}_3^-_{\text{ads}}$ ($30 \text{ cm}^{-1}/\text{V}$) and $\text{HCOO}^-_{\text{ads}}$ ($26 \text{ cm}^{-1}/\text{V}$) were found in Figs. 4 and 5, which denotes weak adsorptions on lead electrode in comparison with those obtained with CO_2 on Pt ($45 \text{ cm}^{-1}/\text{V}$) [56]. Eqs. (6) and (7) are supported by the previous results that we obtained by chromatographic analyses of the electrolyzed solutions, in which formate was the sole reaction product in the bulk solution [57].

It is important to highlight the absence of the band due to carbon monoxide in different spectra. Supplementary *in situ* IR spectra performed with Subtractively Normalized Interfacial Fourier Transform Infrared Reflectance Spectroscopy (SNIFTIRS), which are not shown herein confirm this statement. The spectroscopic results indicate that the electroreduction of hydrogenocarbonate leads selectively to formate on lead electrode in alkaline medium without any intermediate species such as CO.

To support these spectroscopic results, prolonged electrolysis at a lead cathode was carried out using chronopotentiometry ($j = -6.7 \text{ mA cm}^{-2}$) for 3 h with a catholyte containing 150 mL of a 0.5 M KHCO_3 solution (without supply of gaseous CO_2 in the solution). The reduction process was performed in a filter-press

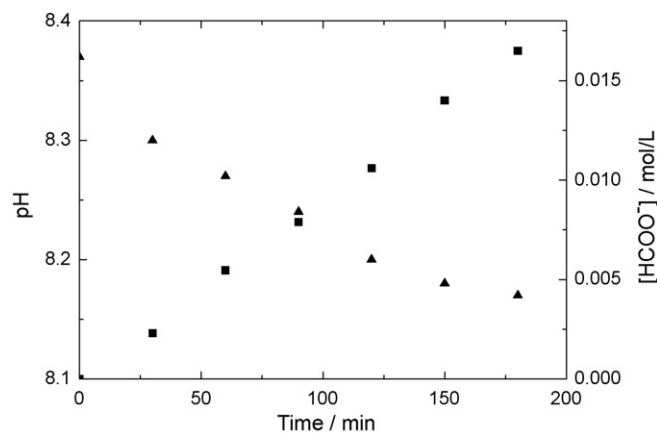


Fig. 8. Evolution of the pH value (▲) and the formate concentration (■) vs. time during current controlled electrolysis (-6.7 mA cm^{-2}) of a 0.5 M KHCO_3 solution at a Pb electrode in a filter-press cell at 21°C .

and quantification was performed via a HPLC analysis, as previously described [57]. The results are shown in Fig. 8. Formate has been detected as the sole reaction product in solution (Faradaic efficiency: 44%). The pH value which was initially measured at 8.37 decreases slowly down to 8.17, while the electrode potential was stabilized at -1.4 V vs. SCE. The partial current density due to formate production is quite high (2.9 mA cm^{-2}), which tends to confirm the spectroscopic results showing that HCO_3^- is the electroactive species.

4. Conclusion

The electroreduction of carbon dioxide was conducted in aqueous and alkaline medium having hydrogenocarbonate ions as predominant species in solution (pH = 8.6 after bubbling CO_2 in a 0.1 M NaOH solution). Taking into account the bands of species present in various spectra obtained with *in situ* IR reflectance spectroscopy, we propose a reaction mechanism of selective hydrogenation of HCO_3^- to HCOO^- . The disappearance of the band ascribed to CO_2 when applying a cathodic electrode potential gives evidence that CO_2 is not absorbed nor is it the electroreducible species on the lead electrode surface. Accordingly, formate was the exclusive organic species identified from HCO_3^- reduction during chronoamperometry/FTIRS experiments at -1.6 V vs. SCE in aqueous or deaerated medium.

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